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EFFECTS OF CYCLIC HEATING AND THERMAL SHOCK ON HAFNIA STABILIZED WITH CALCIA, MAGNESIA, AND YTTRIA*

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SUMMARY

The need for thermal-shock-resistant refractories, used as structures or as a protective coating on aerospace vehicles, initiated an investigation of $\text{HfO}_2\text{-CaO}$, $\text{HfO}_2\text{-Y}_2\text{O}_3$, and $\text{HfO}_2\text{-MgO}$ solid solutions. This study included (1) an investigation of the effect of temperature on the stabilization qualities (stabilization is the process of eliminating or limiting the monoclinic-tetragonal crystallographic inversion common in hafnia at $\approx 1700^\circ\text{C}$) of calcia, yttria, and magnesia in solid solution with hafnia; (2) a determination of the effect of cyclic heating on the crystal lattice stability of solid solutions; and (3) an observation of the effects of thermal shock on partially and fully stabilized hafnia.

Sintering temperature influences the solubility of calcia, yttria, or magnesia in hafnia. Calcia-stabilized hafnia specimens exhibited similar solubility when sintered at 2000°C and at 1800°C . Yttria-stabilized hafnia specimens indicated that sintering temperatures of 2000°C and times longer than 9 hours were necessary to obtain near-maximum solution. The high vapor pressure of magnesia limits sintering temperatures for magnesia-stabilized specimens to 1800°C .

Yttria-stabilized hafnia specimens maintain their stability, whereas magnesia- and calcia-stabilized specimens destabilize when subjected to a single heat cycle (25°C to 1750°C). Reheating destabilized specimens to 1925°C for 30 minutes under 10^{-5} torr (0.00133 N/m^2) did not produce restabilization.

Cyclic heat treatment showed that hafnia stabilized with calcia or yttria maintained original stability when subjected to 25 cycles between 1040°C and 1730°C in air at ambient pressure. Magnesia-stabilized hafnia was stable when removed from the furnace at 1730°C and cooled in ambient air, but was unstable when removed from the furnace at 1040°C and cooled under the same conditions.

The overall thermal-shock resistance of yttria-stabilized hafnia quickly cooled in ambient air from temperatures up to 2000°C was superior to hafnia stabilized with calcia or magnesia.

*The information in this paper was included in a dissertation submitted by John D. Buckley in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Ceramic Engineering, Iowa State University, Ames, Iowa, June 1968.

INTRODUCTION

Prior to the advent of supersonic and hypersonic vehicles, materials used in constructing aircraft were made exclusively of metals. It was assumed that refractory metal alloys and superalloys could be developed to function as required at the elevated temperatures and thermal stresses imposed by flight at hypersonic speeds. Experimental evidence, however, shows that even the best metallic combinations undergo drastic reductions in strength and become susceptible to oxidation and creep at temperatures considerably lower than would occur in aerospace vehicles. (See refs. 1 to 5.)

Materials selection for hypersonic flight is influenced primarily by the temperature profile that a vehicle experiences while cruising at hypersonic velocities or entering the more dense atmosphere near the earth's surface. Figure 1 is a typical temperature profile for a vehicle cruising at Mach 8 at an altitude of 88 000 feet (26 822 meters) above the earth's surface. (See ref. 1.) The wide range of temperatures over the surface of the aerospace vehicle requires selection of the best available material that is compatible with a specific temperature environment (fig. 2) and still maintains structural integrity. (See refs. 3, 5, and 6.)

Correlation of figures 1 and 2 shows that there are specific structural members on a hypersonic vehicle that require ceramics or the equivalent of a ceramic because of the extreme temperatures and oxidizing atmosphere when in flight. The nose cap and leading edges are the areas on these vehicles where melting temperatures and protection from oxidation are extremely critical. (See fig. 1.) Numerous designs, materials, and combinations of materials have been considered for use in these areas. The concepts that have shown the most promise are:

- (1) Protective coatings for graphite and refractory metals (refs. 7 to 11)
- (2) Protective coatings resulting from oxidation of a base metal in an alloy (refs. 11 to 17)
- (3) Ceramic-metal structural composite materials (refs. 18 to 20)

The basic principle of protection for the critical areas of aerospace vehicles against high temperature and oxidizing atmospheres in all these concepts is the construction of a high-temperature thermal barrier made of a superrefractory oxide or the use of a protective oxide coating. The coating is either applied to the surface of the structural member or is the product of thermochemical oxidation. This oxidation is caused by air friction heating of the refractory metal structural surfaces. (See leading edges, fig. 1.)

The extreme thermal and environmental stresses that the nose cap and leading-edge structures of aerospace vehicles encounter when cruising at hypersonic velocities limit the refractory oxides that can be used in these areas to thoria, hafnia, and zirconia.

(See ref. 11.) These oxides (1) have the highest melting temperature of the superrefractory oxides, (2) can be used in oxidizing atmospheres exceeding 2500° C, and (3) have low vapor pressures and low reactivity with most metals. (See refs. 21 to 23.) However, they also have low thermal conductivity and high or erratic thermal expansion. For these reasons they have fair-to-poor resistance to thermal shock. (See refs. 21 to 28.)

The extreme and rapid changes in temperature experienced by ceramic structures and coatings used on aerospace vehicles make thermal shock and spalling, resulting from thermal shock, the most critical parameters with which to cope. (See refs. 19, 20, and 25.) Improvements have been made in the thermal-shock quality of superrefractories by modifying compositions and/or incorporation of unique metal ceramic designs, the purpose being to increase thermal conductivity and decrease thermal expansion. (See refs. 20, 21, 25, 26, and 29 to 32.) The need for even greater improvement in the thermal-shock quality of superrefractories used as structures or as protective coatings on aerospace vehicles was the impetus for the investigation of stabilized hafnia.

Hafnia has a melting temperature of 2800° C, about 100° C higher than zirconia. (See refs. 21, 33, and 34.) In its pure form, hafnia has greater thermal conductivity and less overall thermal expansion than either thoria or zirconia (refs. 24, 25, 27, 32, and 35), and thus has better thermal-shock qualities. Hafnia, however, exhibits a destructive crystallographic transformation (monoclinic-tetragonal) but at a much higher temperature (approximately 1700° C) than zirconia (approximately 1000° C). The transformation of hafnia occurs over a smaller temperature range and with less thermal stress. (See refs. 24 to 28.) Hafnia sintered at elevated temperatures with magnesia, calcia, or yttria is a solid solution with a cubic crystal structure. This material is, like stabilized zirconia, free of crystallographic inversion. It has, however, a linear thermal expansion equivalent to, or greater than, thoria or stabilized zirconia. (See refs. 25 and 27.) Partially stabilized hafnia tends to have a small and gradual overall thermal expansion similar to zirconia. (See refs. 21 and 25.) Partially stabilized hafnia should be higher in thermal conductivity since pure hafnia has a higher thermal conductivity than either thoria or zirconia. (See ref. 24.) This combination of thermal qualities indicates that hafnia could have better thermal-shock resistance than either thoria or zirconia. The many similar properties of hafnia and zirconia suggested use of calcia, magnesia, and yttria as stabilizing agents since they are the oxides most used in the stabilization of zirconia. (See refs. 21, 23, 32, and 34.)

The specific objectives of this investigation were (1) to determine the effect of composition on the degree of stabilization of hafnia, (2) to study the effect of cyclic heating on the stability of solid solutions of hafnia, and (3) to observe the thermal-shock qualities of stabilized hafnia specimens subjected to various heat treatments and rapid cooling.

SYMBOLS

I_{Ca}	X-ray diffraction intensity of calcium
I_c	X-ray diffraction intensity of cubic crystals
I_{Hf}	X-ray diffraction intensity of hafnium
I_{Mg}	X-ray diffraction intensity of magnesium
I_m	X-ray diffraction intensity of monoclinic crystals
I_Y	X-ray diffraction intensity of yttrium
K_α	characteristic X-radiation from the K-shell
L_α	characteristic X-radiation from the L-shell
2θ	angle between diffracted X-ray beam and transmitted X-ray beam
CaO	calcium oxide (calcia)
HfO ₂	hafnium oxide (hafnia)
MgO	magnesium oxide (magnesia)
Y ₂ O ₃	yttrium oxide (yttria)
ZrO ₂	zirconium oxide (zirconia)

The units used for the physical quantities in this paper are given both in U.S. Customary Units and in the International System of Units (SI) (ref. 36). Factors relating the two systems are given in the appendix.

MATERIALS AND SPECIMEN PREPARATION

Materials

The suppliers' certified chemical analyses of the materials are given in table I. All as-received powders were -325 mesh. The compositions investigated were hafnia-calcia,

hafnia-yttria, and hafnia-magnesia, as shown in table II. The oxide components making up each 100-gram composition were weighed on a balance that permitted an accuracy of 0.01 percent or better.

Specimen Preparation

Dry mixing of powders was done in a 1/2-pint (237 cm³), $2\frac{7}{8}$ -inch-diameter (7.3 cm) rubber-lined steel jar mill. A charge consisted of 100 grams of a given mixture and 12 alumina cylinders 1/2 inch in diameter (1.27 cm) by 1/2 inch (1.27 cm) long. Each composition was mixed for 20 hours on a two-roll mill at 24 rotations per minute.

Sintered specimens used for composition-analysis, cyclic-heating, and thermal-shock tests were fabricated by mixing premixed compositions with 5-percent distilled water and 2-percent dextrin, and then cold-pressing in a 3/4-inch-diameter (1.91 cm) die at 27 ksi (186 MN/m²). This die featured a segmented conical insert to facilitate removal of the specimens. (See fig. 3.)

Upon completion of sintering, disk specimens were either mounted and polished for examination in an electron microprobe X-ray analyzer or ground to -325 mesh and analyzed with X-rays. Packed and loose powder specimens were used for X-ray diffraction and fluorescent analysis, respectively, whereas liquid-media powder specimens evaporated on resistance-heated metal foil elements were used for high-temperature X-ray diffraction cyclic-heating analysis. (See fig. 4.)

Microprobe specimens were mounted in bakelite and ground successively with 120-, 240-, 320-, 400-, and 600-grit silicon carbide papers with water as a coolant and polished mechanically with 6-micron diamond paste and diamond extender on a disk polisher. Final polishing was accomplished on a vibratory polisher by using 0.3-micron alumina suspended in distilled water. Upon completion of polishing, all microprobe specimens were coated with a thin carbon film, approximately 200 Å thick, to provide a discharge path for sample current.

X-ray diffraction specimens were prepared by lightly pressing -325 mesh powders in an aluminum holder, by using a piece of glazed tile on one side of the opening and applying pressure with a flat metal knife on the opposite side to alleviate preferred orientation.

Specimens used for X-ray fluorescent analysis were -325 mesh powders loosely packed in cylindrical specimen holders. The bottom surface of the holders had circular 1/4-mil polyethylene-terephthalate windows through which the radiation impinged on the specimens.

High-temperature X-ray diffraction cyclic-heating specimens were prepared by evaporating one or more drops of a suspension of powder in 100-percent ethyl alcohol on

a resistance heater specimen support. (See fig. 4.) Sample thickness was controlled by building up several thin layers obtained by allowing several successive drops to evaporate.

APPARATUS AND PROCEDURE

Sintering

A cold-wall, 2000° C controlled atmosphere or vacuum furnace was used for sintering. An oxidizing atmosphere at temperatures up to 2000° C was accomplished in this furnace by utilizing an open-end, gas-tight refractory oxide tube (stabilized zirconia or alumina) sealed on the outer diameter at both ends and heated by a tantalum element bathed in argon. (See fig. 5.)

To obtain temperature measurements in the cold-wall furnace, a micro-optical pyrometer, including its optics and the quartz sight window located in the furnace wall, was calibrated against a tungsten lamp standard. Control thermocouples located near the maximum heat zone and the micro-optical pyrometer were also calibrated against a platinum—platinum-13-percent-rhodium thermocouple which was positioned in the hot zone of the furnace. At equilibrium and within the upper temperature limit of the platinum—platinum-13-percent-rhodium thermocouple, a variation of less than 10° C was noted between the thermocouple and the micro-optical pyrometer.

Specimens were sintered at 1600° C, 1800° C, or 2000° C for 9 hours in the cold-wall furnace. Three different heating schedules were used. Specimens were either (1) placed in the furnace cold, heated to the desired sintering temperature, soaked, and then cooled to room temperature in the furnace; (2) placed in the furnace at room temperature, heated to the desired sintering temperature, soaked, then withdrawn, and cooled in air to room temperature; or (3) placed in the furnace at the sintering temperature, soaked, withdrawn, and cooled in air to room temperature.

Insertion of specimens into the cold-wall furnace entailed movement of a pedestal up the vertical tube to the upper exit of the furnace by means of a ceramic push rod inserted through the exit at the bottom of the furnace, placing the specimens on the pedestal surface, and then lowering the pedestal to the original position. (See fig. 5.) The same procedure was used for removing specimens. Scrap material of the same composition as that of the specimen was used as a buffer between the specimen and the pedestal surface to prevent contamination.

Cyclic-heating tests and thermal-shock tests were performed in the cold-wall furnace. In the cyclic-heating tests, specimens were placed in the test furnace cold and heated to 1730° C at a rate of 11.5° C per minute. Cycling was done in air between 1040° C and 1730° C for 2, 10, and 25 cycles at a furnace heating and cooling rate of

11.5° C per minute. After the second, tenth, and twenty-fifth cycle, specimens were removed at either 1730° C, or 1040° C, or allowed to cool to room temperature in the furnace; they were then examined at room temperature in the X-ray diffractometer.

Thermal-shock tests were also carried out in the cold-wall furnace. These tests were performed to show the relative merit of the various stabilized hafnia compositions in regard to decreasing thermal-shock resistance resulting from crystallographic inversion. Specimens were inserted into the hot zone, preheated to 2000° C, 1750° C, or 1040° C, soaked for 15 minutes, removed from the furnace, and then cooled to room temperature in air.

Room-Temperature X-Ray Diffraction Studies

X-ray diffraction studies were made in a General Electric XRD-5 diffractometer by using nickel-filtered copper K_{α} radiation. The ratio of the amount of cubic phase to monoclinic phase solid solution (fig. 6), which was a function of the amount of oxide addition in solid solution with HfO_2 , was (as with ZrO_2 , refs. 37 and 38) used as a measure of stabilization. HfO_2 has monoclinic and cubic lattice parameters as well as sintering and inversion behavior closely resembling ZrO_2 . (See refs. 34, 38, 39, and 40.) Hafnia, completely stabilized, contained 100-percent cubic material. Three standardization curves were plotted to show the relationship between the degree of stabilization and the ratio of X-ray diffraction intensities of cubic hafnia completely stabilized with MgO , CaO , or Y_2O_3 , and monoclinic hafnia.

To get as true a relationship as possible between the X-ray intensity measurements of the monoclinic and cubic hafnia peaks, the cubic materials used to obtain data for the standard curves were limited to mixtures in which oxide additions needed for complete stabilization of hafnia were minimal. The minimal oxide additions necessary to produce 100-percent cubic-phase hafnia were determined by X-ray analysis of the various compositions in table II within the sintering temperature and sintering time limit discussed under "Sintering" and are given in the following table:

Weight, percent, of –		Mole, percent, of –	
HfO_2	Additive	HfO_2	Additive
95.0	5.0 CaO	83.5	16.5 CaO
97.0	3.0 MgO	86.0	14.0 MgO
88.0	12.0 Y_2O_3	88.7	11.3 Y_2O_3

HfO_2 - CaO and HfO_2 - Y_2O_3 mixtures were sintered at 2000° C for 9 hours in air at ambient pressure. Because of volatilization due to the high vapor pressure of MgO , HfO_2 - MgO mixtures were sintered at 1800° C for 9 hours in air at ambient pressure. (See ref. 23.)

The standard curves for the quantitative determination of cubic and monoclinic hafnia, as presented in figure 7, are peculiar to the material used in this investigation. These curves were established under specific experimental conditions by using material of a given purity. General analysis can be made with these curves when the procedures and purity of material are similar to those found in this paper. If, however, the purity of the hafnia, calcia, magnesia, and yttria and/or the experimental procedure vary considerably, then new standard curves should be plotted.

Pure cubic and monoclinic hafnia were mixed in proportions of 0 to 100 percent of each in increments of 10 weight percent. An average of 10 specimens was used to determine each point on the curves. Qualitative analysis was accomplished by fast scanning powder specimens at 2° 2θ per minute from $2\theta = 15^\circ$ to $2\theta = 110^\circ$ and comparing the d-spacings with the ASTM card file or selected references (refs. 34, 39, and 40). Quantitative data for plotting the standard curves were obtained by scanning at 0.2° 2θ per minute over the major monoclinic (111) peak ($2\theta \approx 28^\circ$) and cubic (111) peak ($2\theta \approx 30^\circ$) and then measuring their integrated intensities (fig. 6). This measurement was made by drawing a smooth outline over the monoclinic and cubic peaks and tracing them with a planimeter. The I_c/I_m ratio was then plotted against the cubic-monoclinic mixture it represented between 0 and 100 percent. The procedure used for determining the stabilization of known oxide compositions having unknown degrees of solid solution entailed obtaining the I_c/I_m ratio as described and using the appropriate standard curve.

High-Temperature X-Ray Diffraction

A Materials Research Corporation high-temperature diffractometer attachment, model X86-G, was used in conjunction with a 2-inch-diameter (5.08 cm) vacuum system and the General Electric XRD-5 diffractometer arrangement described. This facility was used as a supplement to the cold-wall furnace tests for investigating the effect of cyclic heating on the stabilized hafnia bodies. The heating-element specimen holders (fig. 4), used in the diffractometer furnace, were all made of 0.003-inch-thick (0.00762 cm) 10-percent tantalum, 90-percent tungsten foil. Bragg reflections of specific compositions measured in the room-temperature diffraction investigation were used as gages in zero positioning specimens in the high-temperature X-ray diffractometer. Translation, azimuth, and inclination controls were used to set the diffractometer to the angle at which the specimen's strongest Bragg reflections were known to occur. The specimens were then scanned in air and in a vacuum to make sure that the peak intensities appeared at the anticipated Bragg angles. Power to the ribbon resistance-heater element was not activated until a vacuum of 10^{-4} torr (0.0133 N/m²) was obtained in the X-ray furnace.

Upon establishing the approximate temperatures at which inversion appeared and disappeared with an initial run, each specimen was cycled three or four times. When thermal cycling caused hafnia solid solutions to destabilize rapidly, five or more specimens of the same composition were used to identify the temperature limits of the inversion. Hafnia specimens, destabilized because of cyclic heating in the X-ray furnace, were heated to the temperature limit of the X-ray furnace, soaked for 30 minutes, and cooled rapidly in the furnace to determine whether restabilization, as in ZrO_2 (ref. 41), could be accomplished. Quantitative changes of the phases present resulting from particular heating schedules were determined by soaking the specimen from 5 to 10 minutes at specific temperatures, scanning the specimen with the X-ray diffractometer between 25° and 35° at 2° 2θ per minute, and noting gross changes in or the absence of I_c/I_m ratios.

Temperature measurements in the X-ray diffraction furnace were made with a micro-optical pyrometer (0.65 micrometer). As stated by Wolten (ref. 42), diffracted X-ray beams are from the top layer of the specimen at an average depth of 0.05 mm or less. Therefore, temperatures measured optically on the specimen surface are considered to be most representative of the true temperatures associated with a given diffraction pattern. Pyrometer optics, the furnace sight glass, and prism absorption corrections were determined by calibrating the entire system with a tungsten lamp standard under simulated operating conditions. An emittance value of 0.75 was used for hafnia. (See refs. 24, 25, and 43.)

X-Ray Fluorescent Analysis

X-ray fluorescent analysis was accomplished in a Phillips universal vacuum X-ray spectrograph using tungsten X-radiation and a lithium fluoride crystal. The procedure used to measure the calcia and yttria added to hafnia was similar to that used in obtaining percent stabilization. Integrated intensity ratios of $I_{\text{Ca}}/I_{\text{Hf}}$ and $I_{\text{Y}}/I_{\text{Hf}}$ were plotted against the compositions they represented to produce calcia (fig. 8) and yttria (fig. 9) calibration curves. Data for plotting these curves were obtained by scanning the L_α peak for hafnia and the K_α peaks for calcia and yttria at 0.25° 2θ per minute. All the compositions used in obtaining data for the standard $\text{HfO}_2\text{-CaO}$ and $\text{HfO}_2\text{-Y}_2\text{O}_3$ curves were sintered at 1600°C for 9 hours prior to fluorescent analysis. Subsequent fluorescent analyses were made on $\text{HfO}_2\text{-CaO}$ and $\text{HfO}_2\text{-Y}_2\text{O}_3$ compositions sintered at 1800°C for 9 hours to observe the effect of temperature on the loss, if any, of major components in a specific composition. Because the X-ray spectrometer was unable to detect magnesium in these specimens, an electron microprobe X-ray analyzer was used to determine the magnesia standard curve in the $\text{HfO}_2\text{-MgO}$ compositions. (See fig. 10.)

Electron Microprobe X-Ray Analyses

Electron microprobe X-ray analyses were performed in an Applied Research Laboratory model EMX electron microprobe X-ray analyzer using lithium fluoride and ADP crystals. Specimens used in this investigation were subjected to the same sintering treatment as the specimens used for X-ray fluorescent analysis. A standard curve was constructed for use in the qualitative analyses of $\text{HfO}_2\text{-CaO}$ and $\text{HfO}_2\text{-MgO}$ compositions. It was produced by correlating integrated intensity ratios of $I_{\text{Ca}}/I_{\text{Hf}}$ and $I_{\text{Mg}}/I_{\text{Hf}}$ calculated from microprobe data and plotted against known quantitative values of the compositions they represented. The procedure for determining compositions sintered at higher temperatures and longer times was the same as that used in the X-ray fluorescent analyses. Data for plotting standard curves were obtained by scanning the L_{α} peak for hafnium with a lithium fluoride crystal, the K_{α} peaks for calcium with a lithium fluoride crystal, and the K_{α} peak for magnesium with an ADP crystal at a speed of $0.2^{\circ} 2\theta$ per minute.

RESULTS AND DISCUSSION

Room-Temperature X-Ray Diffraction Studies

Stabilization is a process that has been found to eliminate or reduce the deleterious effect of the monoclinic-tetragonal inversion experienced by hafnia bodies in the neighborhood of 1700°C . (See refs. 27 and 28.) The stabilization process consists of mixing and sintering specific oxides with hafnia, such as shown in table II, to form solid solutions. These solid solutions have a cubic crystal structure which is believed to be stable.

As inferred in the introduction of this paper, the right combination of the cubic and monoclinic phases could, like zirconia (ref. 26), produce a specimen with improved thermal-shock qualities. Figure 7 shows the ratio of intensity of cubic phase to intensity of monoclinic phase derived from X-ray diffraction data plotted against measured amounts of cubic phase added to monoclinic-phase hafnia. These curves were used as standards to analyze quantitatively partially stabilized specimens subjected to various and/or repeated heat treatments.

In figure 7, the $\text{HfO}_2\text{-CaO}$ and $\text{HfO}_2\text{-MgO}$ cubic-phase additions to monoclinic hafnia displayed similar curves through most of their length. The $\text{HfO}_2\text{-Y}_2\text{O}_3$ cubic-phase additions to monoclinic hafnia, however, showed higher $I_{\text{c}}/I_{\text{m}}$ ratios than either of the other compositions along the entire length of the curve. The differences observed between the curves in figure 7 were attributed to the way and degree that the diffractions of X-rays were affected by the atoms making up the cubic-phase solid solutions mixed with monoclinic hafnia. Every atom has, among other factors (ref. 44), a characteristic scattering and absorption factor which influences the relative intensity of lines on X-ray diffraction

powder patterns. The differences noted in the atomic number and, thus, the scattering factor of the substituted cations in the hafnia solid solutions, explain to some degree the reason that hafnia stabilized with the same mole percent of CaO, MgO, or Y₂O₃ had different I_c/I_m ratios.

Figures 11 to 13 present results that show the variation in the production of cubic hafnia with sintering temperature for the compositions listed in table II. The calcia-stabilized hafnia plots (fig. 11), in which sintering time was held constant while the temperature was varied, show that temperature had little or no influence on the amount of cubic phase formed for any given weight percent addition of calcia to hafnia. The close proximity of the curves and overlapping points of figure 11 indicate that sintering for 9 hours at 1800° C was sufficient to obtain maximum solution in the 1800° C to 2000° C temperature range.

The data used in plotting these curves were obtained from values calculated from X-ray diffraction patterns of specimens heated and cooled slowly in the cold-wall furnace (2° C per minute). To determine whether the heating schedule influenced stabilization, specimens were heated slowly and removed at sintering temperatures and also put in and removed at sintering temperatures. X-ray evaluation of specimens subjected to these heat treatments exhibited no variation from specimens heated and cooled slowly.

The increasing slopes of the 1800° C and 2000° C curves in figure 12 exhibit the strong influence of temperature on the formation of cubic hafnia with yttria additions. The absence of overlap in the upper portion of the curves in figure 12 is in direct contrast to the overlap observed in the calcia-stabilized hafnia curves. (See fig. 11.) It is believed that the overlap in the calcia-stabilized hafnia indicates that complete solid solution has been achieved whereas the absence of overlap in the curves of figure 12 indicates the presence of free yttria. This condition suggests the need for sintering yttria additions to hafnia at temperatures higher than 2000° C or periods of time longer than 9 hours to obtain maximum solution.

The amount of cubic hafnia as a function of weight percent magnesia addition to monoclinic hafnia curve, shown in figure 13, was initially considered not plottable because of the erratic X-ray diffraction data obtained from sintered specimens heated and cooled slowly (11.5° C per minute) in the cold-wall furnace. However, specimens heated to sintering temperature, soaked, and then removed and cooled to room temperature in air produced X-ray diffraction specimens that gave repeatable patterns. This repeatability allowed the calculation of I_c/I_m ratios, and thus the plotting of figure 13. It is reasonable from these observations to predict that magnesia comes out of solution when cooled slowly and is frozen in solution when cooled quickly.

Except for the 3-percent additions, the X-ray diffraction patterns of magnesia-stabilized hafnia sintered at 2000° C were erratic. The erratic data are believed to

result from a loss of magnesia due to vaporization. (See ref. 21.) The points representing the 3-weight-percent additions of magnesia to hafnia in figure 13 show that the amount of cubic hafnia formed at a sintering temperature of 2000° C is less than at 1800° C for the same sintering time. This decrease in stabilization with increased sintering temperature is opposite to that observed in the calcia and yttria stabilization processes.

To substantiate the supposition that magnesia was vaporizing, microprobe analyses were performed on hafnia bodies containing 1, 2, 3, and 5 weight percent magnesia sintered at 2000° C for 9 hours in air. They showed a loss of approximately 1 weight percent magnesia due to the sintering when compared with similar specimens on the standard curve that had been sintered in air for 9 hours at 1600° C. (See fig. 10.) Electron microprobe analyses of magnesia-stabilized hafnia specimens sintered in air for 9 hours at 1800° C showed no difference in amount of magnesia present when compared with similar values on the standard curve.

At least five specimens each of hafnia stabilized with 1-, 2-, 3-, and 4-percent calcia were subjected to X-ray fluorescent analysis after sintering for 9 hours at 2000° C. No noticeable change was observed in the chemical composition of these specimens when compared with the standard curve. (See fig. 8.)

Hafnia stabilized with 3-, 5-, 7-, 12-, and 15-percent yttria was subjected to heat treatment similar to that performed on calcia-stabilized hafnia specimens. The yttria-stabilized hafnia specimens showed no decrease in yttria when compared with the standard curve (fig. 9).

Effect of Cyclic Heating on Stabilization

Cyclic tests in the high-temperature X-ray furnace.- High-temperature X-ray diffraction analysis of stabilized hafnia specimens showed that temperature exerted a strong influence on stabilization. A survey of high-temperature X-ray diffraction patterns of calcia-stabilized hafnia displayed several distinct phase changes taking place when heating and cooling specific calcia-stabilized specimens. Room-temperature X-ray analyses exhibited standard diffraction patterns for 1- and 3-percent calcia additions to hafnia sintered for 9 hours at 2000° C.

The X-ray diffraction patterns of 1-percent calcia-stabilized hafnia showed the (111) monoclinic peak at temperatures up to 1750° C. At 1750° C, all the monoclinic phase transformed to tetragonal phase. Since the major peaks of the tetragonal and cubic phases occupy the same 2θ angles on X-ray patterns, the only evidence of the presence of the tetragonal phase was the noticeable increase in the X-ray peaks common to both phases. On cooling, the monoclinic (111) peak appeared at 1646° C and increased in intensity with decreasing temperature. At room temperature, the 1-percent

calcia-stabilized specimens were predominantly and, in most cases, completely monoclinic in crystal structure; therefore, the heat cycle had produced destabilization.

The 3-percent calcia-stabilized hafnia specimens exhibited changes in X-ray diffraction pattern commencing at approximately 1236°C . These specimens, unlike the 1-percent calcia-stabilized specimens, displayed X-ray patterns where the (111) monoclinic peak increased in intensity and the supposedly stable cubic phase decreased in intensity with increasing temperature. The 3-percent calcia-stabilized hafnia body that showed 95-percent stability at room temperature displayed only 25-percent stability at 1478°C . At 1530°C the (111) monoclinic peak began to decrease in intensity and continued to do so until it disappeared at approximately 1745°C . Because of the large drop in cubic phase between 1236°C and 1478°C , it is believed that dissolution of the cubic phase was taking place; therefore, at temperatures above 1745°C , the tetragonal phase was predominant and some cubic phase may be present. On cooling, the monoclinic (111) peak appeared at 1643°C and, like the monoclinic peaks observed on the 1-percent calcia-stabilized hafnia X-ray patterns, increased in intensity to room temperature. The monoclinic phase and, in rare instances, small amounts of cubic phase were observed on X-ray patterns of these 3-percent calcia specimens at room temperature.

Calcia-stabilized hafnia specimens containing 95-percent cubic phase heated in the X-ray furnace from room temperature to 1925°C in approximately 5 minutes and then cooled to room temperature in about 2 minutes exhibited X-ray patterns, after cooling, that showed complete destabilization in almost all the tests. Room-temperature X-ray patterns of destabilized specimens, heated in the X-ray furnace to 1925°C and soaked for at least 30 minutes and cooled quickly, displayed no change in pattern; thus, vaporization of the free calcia (ref. 45) is suggested or restabilization requires longer sintering times or higher sintering temperatures if sintering is limited to 30 minutes.

Elevated-temperature X-ray analyses of calcia-stabilized hafnia specimens containing 95-percent cubic phase hafnia heated in the X-ray furnace at temperatures ranging between 1100°C and 1300°C showed significant increases in monoclinic hafnia and decreases in cubic phase hafnia. In some cases the cubic phases showed a decrease of as much as 70 percent. Soak time at constant temperature did not affect the intensities of the peaks in any given patterns; however, it was noted that as the temperature was increased from test to test, the amount of cubic phase hafnia present decreased. These observations suggest that destabilization of calcia-stabilized hafnia, like the monoclinic-tetragonal inversion of hafnia, is athermal in nature. (See ref. 42.)

X-ray analysis of 5-percent calcia-stabilized hafnia specimens displayed X-ray diffraction patterns showing only cubic-phase hafnia. Between 1230°C and 1280°C , the X-ray patterns of cubic hafnia resolved into a new pattern representing the destabilization of the cubic hafnia phase. As was observed in the X-ray patterns of the 1- and 3-percent

calcia-stabilized hafnia specimens, the patterns of the 5-percent calcia additions to hafnia showed an overall decrease in the intensity of the (111) tetragonal-cubic peak and an increase in the (111) monoclinic peak as temperatures approached 1530° C. Above 1530° C the opposite was true; the monoclinic peak decreased in intensity, whereas the tetragonal-cubic peak increased in intensity. At 1750° C the monoclinic peaks disappeared, and the only phases present above this temperature were the tetragonal and possibly the cubic phase. On cooling, the monoclinic (111) peak made its appearance at approximately 1646° C. The intensity of the monoclinic peak increased whereas the tetragonal-cubic peak decreased in intensity as the specimen was cooled to room temperature.

Room-temperature X-ray patterns displayed the monoclinic phase and, in some tests, cubic hafnia, and showed complete or almost complete destabilization of the stabilized hafnia as a result of single heat cycles. Heating destabilized hafnia specimens to 1925° C and soaking for 30 minutes followed by quick cooling to room temperature produced no change in the X-ray patterns. At this point in the investigation, it was uncertain whether calcia additions to hafnia vaporized because of the high temperature and the 10^{-5} torr (0.00133 N/m²) vacuum in the X-ray furnace (ref. 21).

The 3-, 5-, 7-, and 12-percent yttria-stabilized hafnia specimens investigated exhibited no change in X-ray diffraction patterns on heating or cooling that would indicate destabilization.

To determine the stability of the yttria-stabilized hafnia bodies, each of the test X-ray diffraction specimens was heated quickly (~10 minutes) to approximately 1925° C and cooled quickly (~2 minutes) 5 times. X-ray analyses made at room temperature before and after each cycle showed little or no change in the intensities and/or the ratio of the (111) cubic and (111) monoclinic peaks. At least three specimens were heated to temperatures just below the endpoint temperature designating termination of the monoclinic-tetragonal inversion. These temperatures were held for 30 minutes, and then the specimens were cooled quickly. Little or no change in the intensity and/or ratio of the (111) cubic and (111) monoclinic peaks was observed on the X-ray diffraction pattern after three cycles per specimen.

Hafnia, stabilized with 2-, 3-, and 5-percent magnesia by heating for 9 hours at 1800° C followed by quick cooling, destabilized when subjected to cyclic heat treatment in the X-ray furnace. X-ray diffraction patterns of all the specimens examined displayed little or no stability when heated to and above 1170° C. Before and after X-ray patterns of specimens quick heated to 1925° C and immediately quickly cooled and specimens soaked at 1925° C for 30 minutes and then quickly cooled provided the same results (that is, complete or almost complete destabilization).

Of the three stabilized hafnia compositions investigated in the high-temperature X-ray diffraction unit, yttria-stabilized hafnia proved to be the only stable solid solution. The calcia- and magnesia-stabilized hafnia bodies suffered decomposition at very low temperatures. Heating for short periods of time (30 minutes) at 1925° C failed to restabilize decomposed cubic phase bodies.

Cyclic test at atmospheric pressure.- Cyclic heating of hafnia specimens stabilized with 2-, 3-, and 5-percent calcia or 3-, 7-, and 12-percent yttria in the cold-wall furnace at 1 atmosphere exhibited little or no change in stability when examined at room temperature by X-ray diffraction after 25 heating cycles between 1040° C and 1730° C. The constancy of stabilization shown by the calcia-stabilized hafnia specimens was in variance with the complete destabilization experienced by similar specimens when examined for amount of cubic phase by X-ray analysis during cyclic heating in the X-ray furnace. It is believed that the calcia-stabilized hafnia specimens maintained their stabilization under the former heating conditions and showed no cubic phase present under the latter conditions because of temperature and atmosphere. Specimens cycled up to 25 times in the cold-wall furnace were heated and cooled from 1040° C to a maximum temperature of 1730° C in 2 hours at ambient pressure. Calcia-stabilized hafnia specimens heated in the X-ray furnace were all heated well above the endpoint temperature of 1750° C to insure completion of the monoclinic-tetragonal inversion and under a vacuum of 10^{-5} torr (0.00133 N/m^2) to prevent oxidation of the 10-percent tantalum, 90-percent tungsten ribbon heating element. As was observed in the high-temperature X-ray results, destabilization of calcia-stabilized hafnia took place at 1230° C. If it is assumed that calcia was in a free state (mixed with hafnia) between 1230° C and some higher restabilization temperature, it is believed that rather than go into solid solution at temperatures in the neighborhood of 1750° C, as would occur at ambient pressure, the calcia vaporized because of the combined effects of a 10^{-5} torr (0.00133 N/m^2) vacuum and the high temperature. (See refs. 21 and 40.) Because of the small size of the ribbon heater specimen, a quantitative analysis of such specimens subjected to cyclic heat treatment in the X-ray furnace was unobtainable. X-ray diffraction patterns of calcia-stabilized hafnia specimens heated at ambient pressure and drawn at 1040° C or 1730° C after 25 cycles showed little or no change in stabilization when compared with patterns of the same specimens examined prior to the cyclic heat treatment.

The yttria-stabilized hafnia specimens were cycled under the same conditions as the hafnia specimens stabilized with calcia. These yttria-stabilized hafnia specimens exhibited small but progressive increases in (111) cubic peak intensity, with increasing cycles, when compared with X-ray diffraction patterns of the same specimens made before the cyclic tests.

The 2-, 3-, and 5-percent magnesia-stabilized hafnia specimens initially produced by quick cooling, described earlier in this paper, went in and out of solution depending on the temperature at which the specimen was drawn from the furnace during a heat cycle. Specimens removed at 1730° C maintained their stability, whereas specimens removed at 1040° C or allowed to cool to room temperature in the cold-wall furnace displayed little or no stabilization.

Thermal-Shock Tests

Tests made on hafnia stabilized with calcia, yttria, and magnesia showed that composition was the primary factor contributing to thermal-shock resistance. (See fig. 14.) Because thermal shock might be influenced by chemical and physical changes such as formation of intermediate compounds and formation and decomposition of solid solutions as well as quick cooling, specimens were withdrawn and cooled in air at temperatures where these reactions typically occur. Thermal-shock failure was characterized by fracture of the specimens.

Comparisons of thermal-shock qualities of hafnia bodies, partially and fully stabilized with CaO, Y₂O₃, and MgO, removed at 1040° C are shown in figure 14(a). These specimens were removed at 1040° C because it was representative of the temperature zone where decomposition of calcia-stabilized hafnia bodies was observed in the high-temperature X-ray diffraction investigation. The yttria-stabilized bodies, particularly those partially stabilized, exhibited the best thermal-shock resistance at this temperature when compared with calcia- and magnesia-stabilized bodies. Since the monoclinic-tetragonal phase transformation of stabilized hafnia bodies is still taking place or is just completed at approximately 1750° C, specimens were withdrawn from the cold-wall furnace and cooled in ambient air to observe the effect of this inversion on thermal-shock resistance. Figure 14(b) shows magnesia and fully stabilized calcia-stabilized hafnia bodies to be poor in resistance to thermal shock compared with hafnia stabilized with yttria and partially stabilized with calcia. The specimens that showed the best resistance to thermal shock were those hafnia specimens highly but not completely stabilized with yttria and calcia. Results similar to figure 14(b) were observed in the 2000° C thermal-shock data displayed in figure 14(c). The effect of the higher temperature, however, caused greater attrition of specimens among the highly stabilized calcia- and yttria-stabilized hafnia specimens after 18 cycles.

The yttria-stabilized hafnia specimens showed the greatest overall resistance to thermal shock. The specimens that maintained their structural integrity (did not fracture) through 25 thermal-shock cycles were the calcia- and yttria-stabilized specimens containing large amounts of cubic phase. These data indicate that hafnia, like zirconia,

partially stabilized with calcia or yttria tends to have better thermal-shock resistance than either the completely cubic phase or the pure monoclinic phase.

SUMMARY OF RESULTS

An investigation of the effect of temperature on the stabilization qualities of calcia, yttria, and magnesia in solid solution, the effect of cyclic heating on the crystal lattice stability of these solid solutions, and the effects of thermal shock on partially and fully stabilized hafnia indicated the following results:

1. Temperature influenced the stabilization of hafnia with calcia, yttria, or magnesia. Calcia-stabilized hafnia bodies displayed degrees of solid solution at 1800° C, similar to bodies that had been sintered at 2000° C for the same period of time. Yttria-stabilized hafnia bodies, however, showed continued increases in stabilization with increasing temperature. The instability of magnesia-stabilized bodies necessitated quick cooling from sintering temperatures to hold the magnesia in solid solution with hafnia.

2. High-temperature X-ray diffraction analysis showed destabilization followed by breakdown into free calcia and monoclinic hafnia with increasing temperature. Rather than go into solid solution with hafnia at elevated temperatures, it is believed that the same calcia vaporized because of the 10^{-5} torr (0.00133 N/m²) vacuum present in the X-ray furnace. The use of magnesia would also be questionable for use in stabilizing hafnia since it also destabilized and vaporized on heating. The yttria-stabilized hafnia specimens maintained the same degree of stabilization up to the inversion temperature. Cycling through and in and out of the inversion zone indicated that HfO₂-Y₂O₃ solid solutions are stable.

3. Calcia-stabilized cubic hafnia specimens exhibited little or no change in degree of stabilization after 25 heat cycles at all test temperatures. Magnesia-stabilization hafnia specimens were destabilized when removed at 1040° C and maintained their stability when removed at 1730° C. Destabilized specimens could be restabilized when heated and cooled quickly from 1730° C. Because of its instability, magnesia is considered to be inadequate as a stabilizer for hafnia.

4. Tests show that yttria-stabilized hafnia specimens have the best overall resistance to thermal shock. Hafnia partially stabilized with yttria (90-percent cubic phase) exhibited the best thermal-shock resistance of all the specimens tested. Hafnia bodies partially stabilized with calcia (70-percent cubic phase) showed very good thermal-shock resistance when cooled in ambient air from 2000° C and 1750° C. The calcia-stabilized hafnia, however, displayed relatively poor thermal-shock resistance when removed at

1040° C. Because of its instability, magnesia-stabilized hafnia had the poorest thermal-shock resistance at all test temperatures.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., April 8, 1969,
129-03-09-05-23.

APPENDIX A

CONVERSION OF U.S. CUSTOMARY UNITS TO SI UNITS

The International System of Units (SI) was adopted by the Eleventh General Conference on Weights and Measures, Paris, October 1960, in Resolution No. 12 (ref. 36). Conversion factors for the units used herein are given in the following table:

Physical quantity	U.S. Customary Unit	Conversion factor	SI Unit
Length	{ ft	*0.3048	m
	{ in.	*0.0254	m
Mass	lbm	*0.4536	kg
Pressure	{ torr	*133.322	N/m ²
	{ ksi	*6.89 × 10 ⁶	N/m ²
Temperature	°C	+273	°K
Volume (U.S. liquid)	pint	*4.73176 × 10 ⁻⁴	m ³

*Multiply value given in U.S. Customary Unit by conversion factor to obtain equivalent value in SI Unit.

Prefixes to indicate multiples of units are as follows:

Prefix	Multiple
mega (M)	10 ⁶
kilo (k)	10 ³
centi (c)	10 ⁻²
milli (m)	10 ⁻³

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TABLE I.- ANALYSES OF SAMPLE MATERIALS

Impurity or property	Concentration, percent, of -			
	HfO ₂ (a)	CaO (b)	Y ₂ O ₃ (c)	MgO (d)
Al	0.0025			
B	.00002			
Ba				0.003
Ca				.05
Cd	.0001			
Cl				.002
Co	.0005			
Cr	.001			
Cu	.004			
Fe	.005			.002
K				.005
Mg	.001			
Mn	.001			.0005
Mo	.001			
Na				.5
Ni	.001			
NO ₃				.005
Pb	.0005			.0006
Si	.004			
Sn	.001			
Sr				.005
Ti	.002			
V	.0005			
W	.002			
Zr	.026			
La ₂ O ₃			nil to trace	
CeO ₂			nil to trace	
Pr ₃ O ₄			nil to trace	
Nd ₂ O ₃			nil to trace	
Sm ₂ O ₃			nil to trace	
Eu ₂ O ₃				
Gd ₂ O ₃			0.01	
Tb ₄ O ₇				
Dy ₂ O ₃				
Nb ₂ O ₃			nil to trace	
Er ₂ O ₃			nil to trace	
Yb ₂ O ₃			nil to trace	
LuO ₃			nil to trace	
CaO			nil to trace	
NH ₄ OH			.004	.006
SO ₄				.002
F		0.001		
Insoluble in dilute HCl				0.01
Soluble in H ₂ O25
Loss on ignition3

^aWa Chang Corporation spectrographic grade, lot RX9639C.^bFisher Scientific Company certified reagent grade, lot 722951.^cConsolidated Astronautics, Inc., lot 0402.^dFisher Scientific Company certified reagent grade, lot 72082.

TABLE II. - COMPOSITION OF OXIDE MIXTURES INVESTIGATED

Weight, percent		Mole, percent	
HfO ₂	CaO	HfO ₂	CaO
99.0	1.0	96.35	3.65
98.0	2.0	92.99	7.01
97.0	3.0	89.60	10.40
96.0	4.0	86.40	13.60
95.0	5.0	83.5	16.5
HfO ₂	MgO	HfO ₂	MgO
99.0	1.0	95.00	5.00
98.0	2.0	90.35	9.65
97.0	3.0	86.0	14.00
95.0	5.0	78.35	21.65
HfO ₂	Y ₂ O ₃	HfO ₂	Y ₂ O ₃
97.0	3.0	97.20	2.80
95.0	5.0	95.30	4.70
93.0	7.0	93.45	6.55
91.0	9.0	91.54	8.46
88.0	12.0	88.70	11.30
85.0	15.0	85.80	14.20

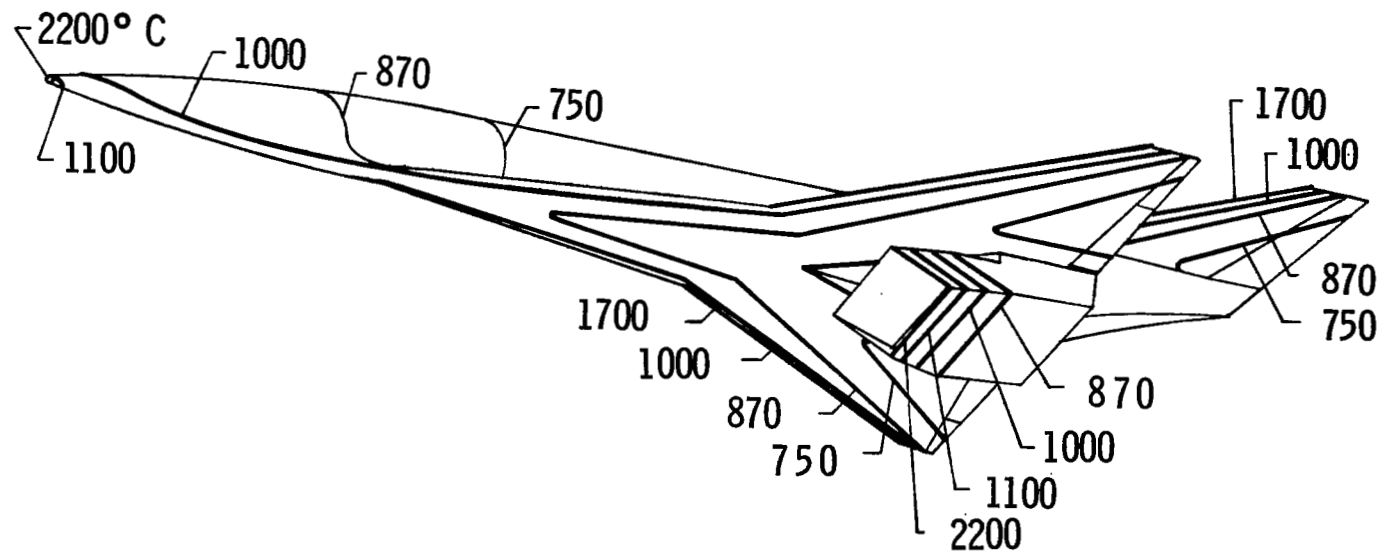


Figure 1.- Equilibrium surface temperatures during sustained flight at Mach 8 at 88 000 feet (26 822 meters). (See ref. 1.)

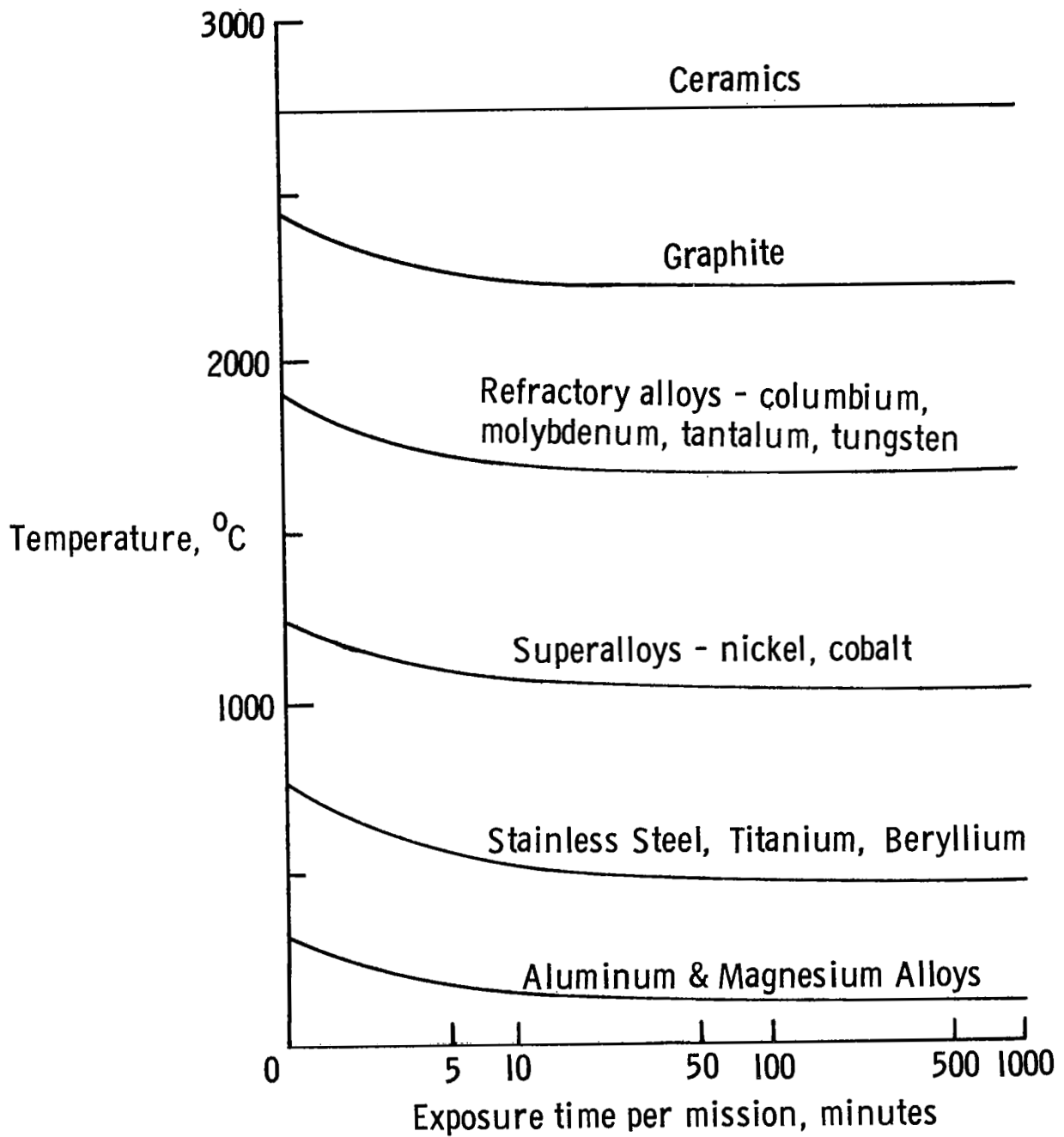


Figure 2.- Potential temperature capabilities for various structural materials. (See ref. 3.)

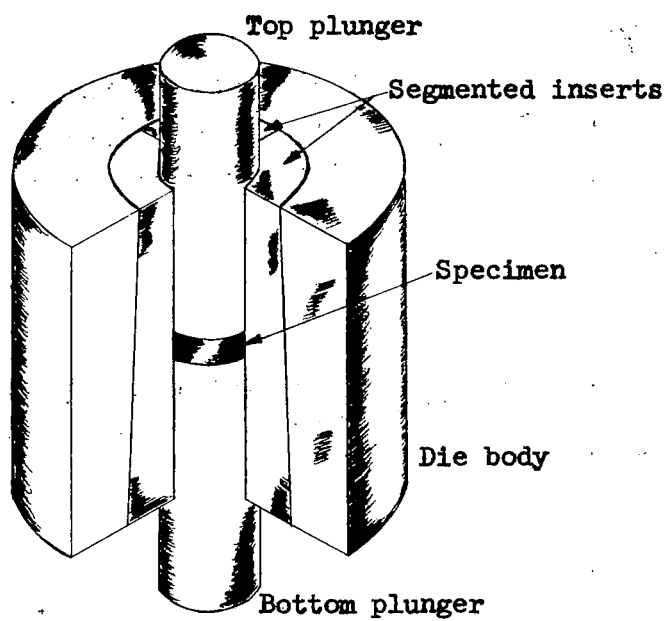


Figure 3.- Double-action split-ring die.

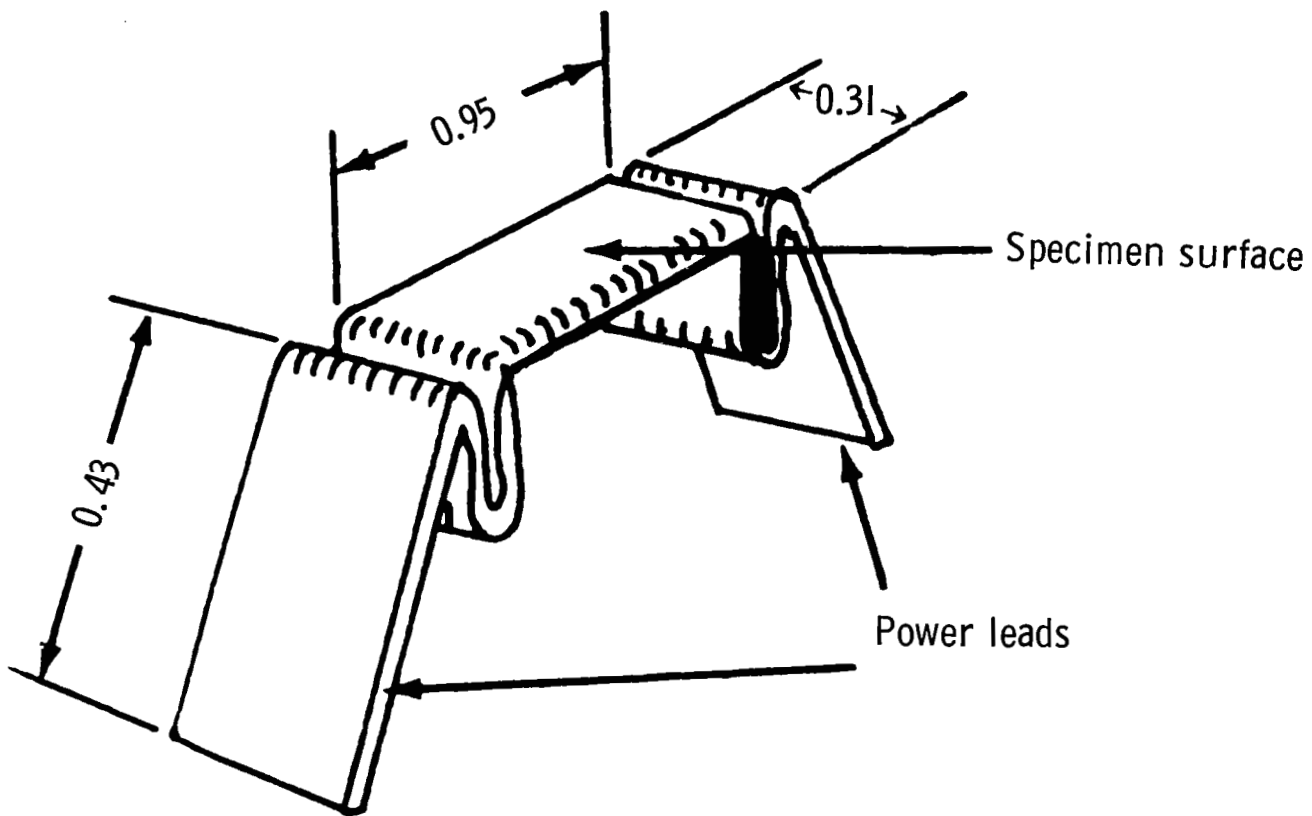


Figure 4.- Heater design for high-temperature X-ray diffractometer attachment. (Dimensions are in centimeters.)

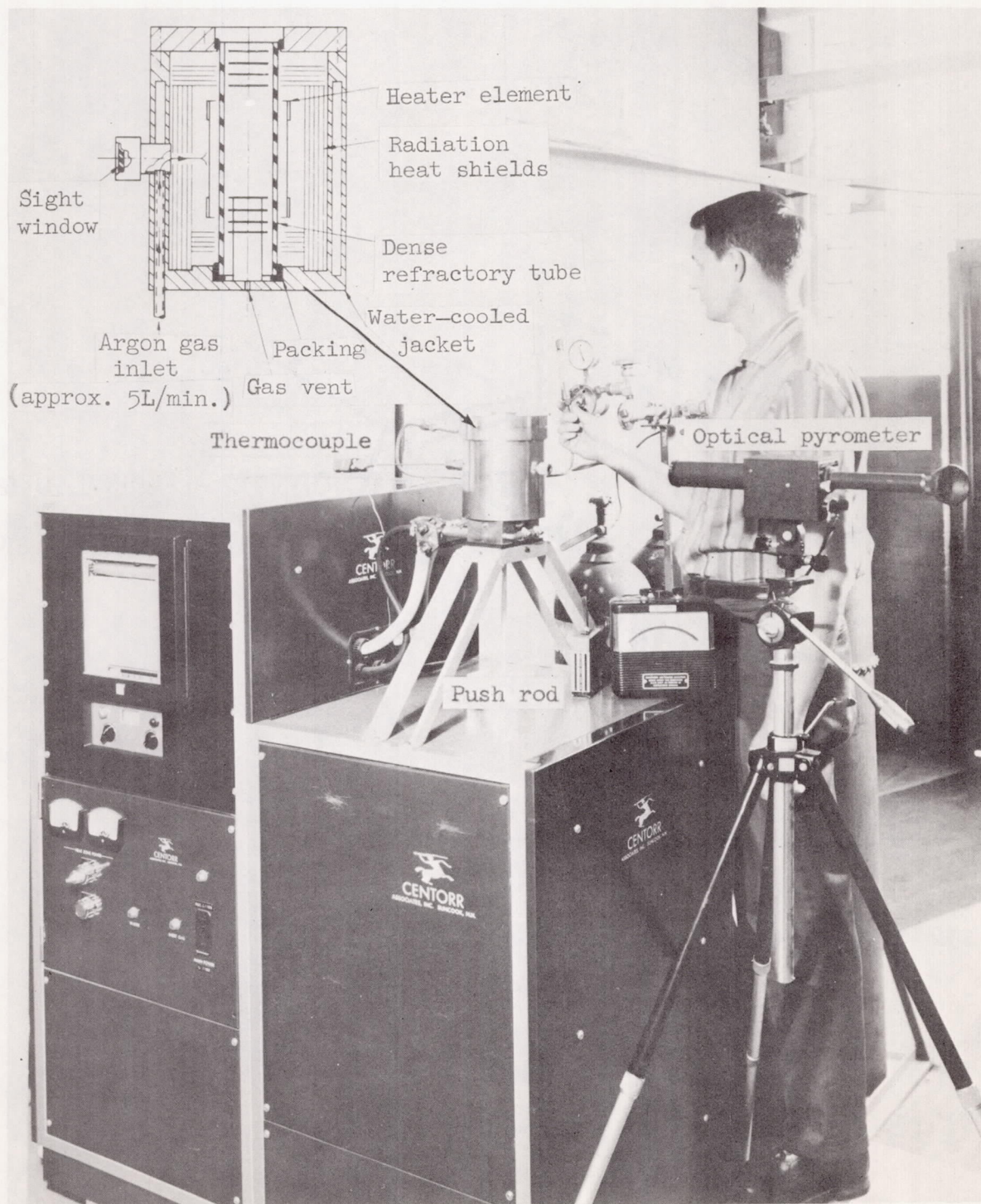


Figure 5.- 2000° C atmosphere (air or inert) and vacuum furnace.

1-69-1353

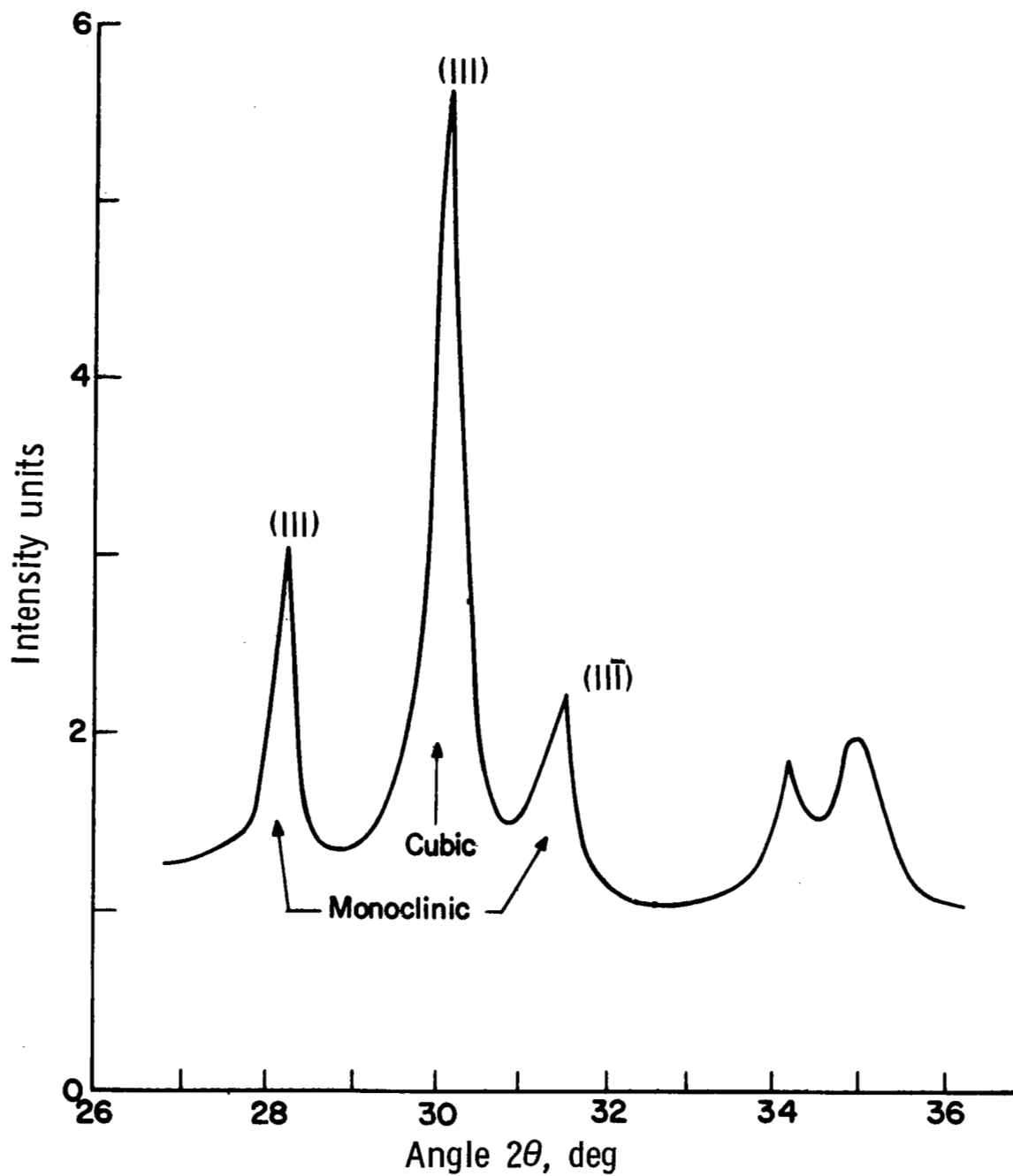


Figure 6.- X-ray diffraction curve for 60-percent cubic-40-percent monoclinic hafnia. (Calcium stabilized.)

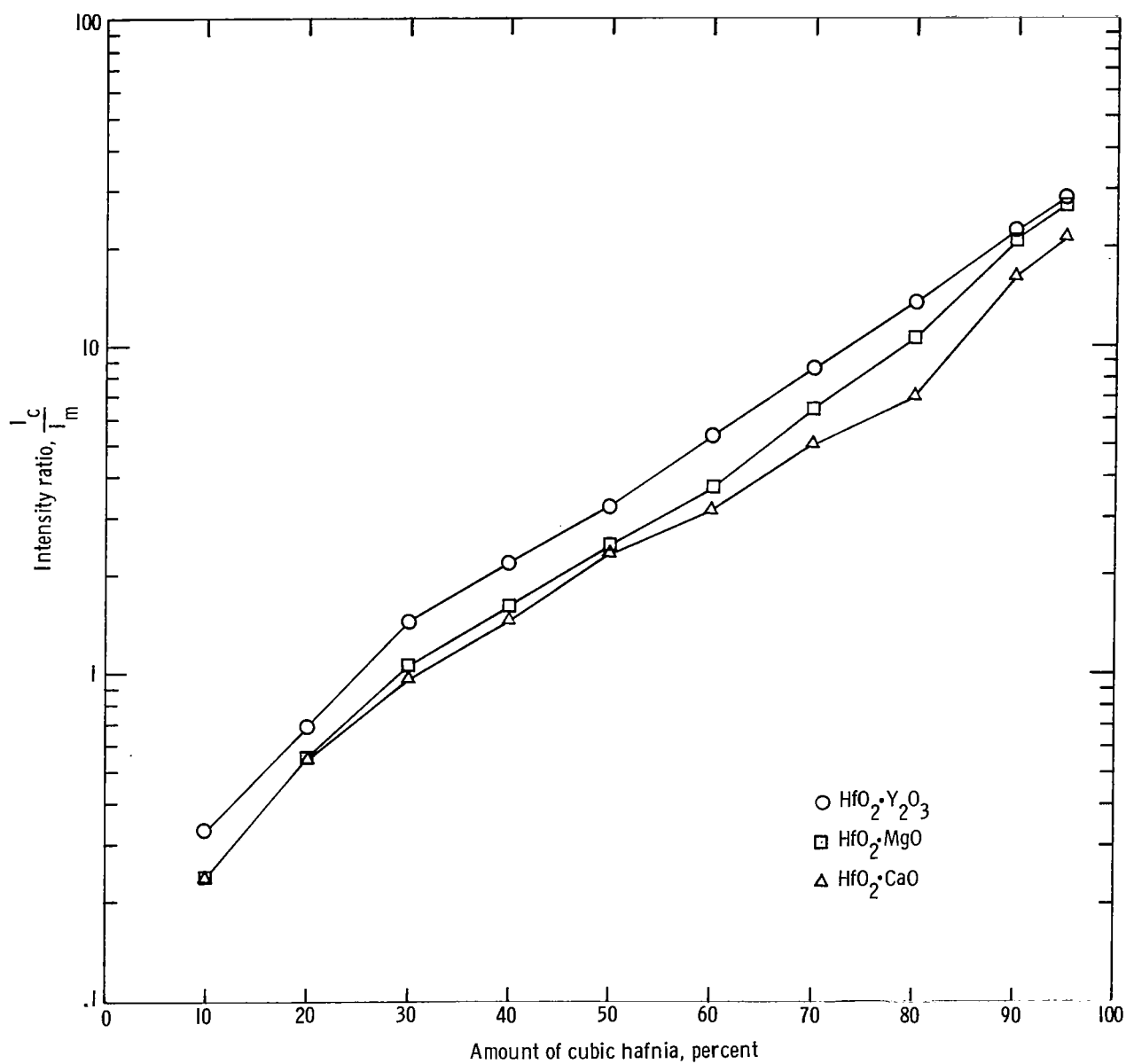


Figure 7.- Ratio of intensity of (111) cubic line to (111) monoclinic as a function of percentage of cubic hafnia.

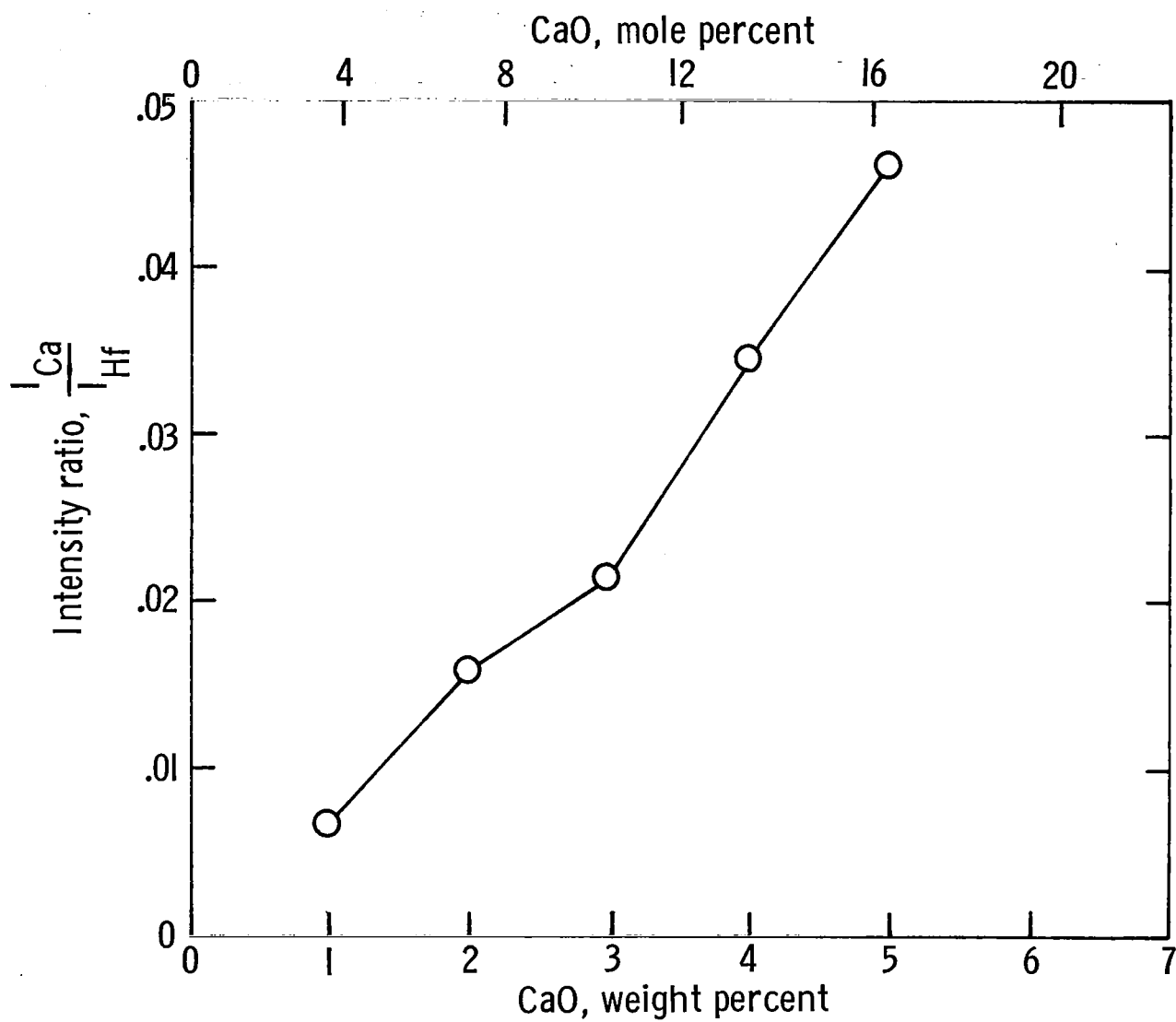


Figure 8.- Standard curve for determination of calcia content in hafnia using X-ray fluorescent analysis.

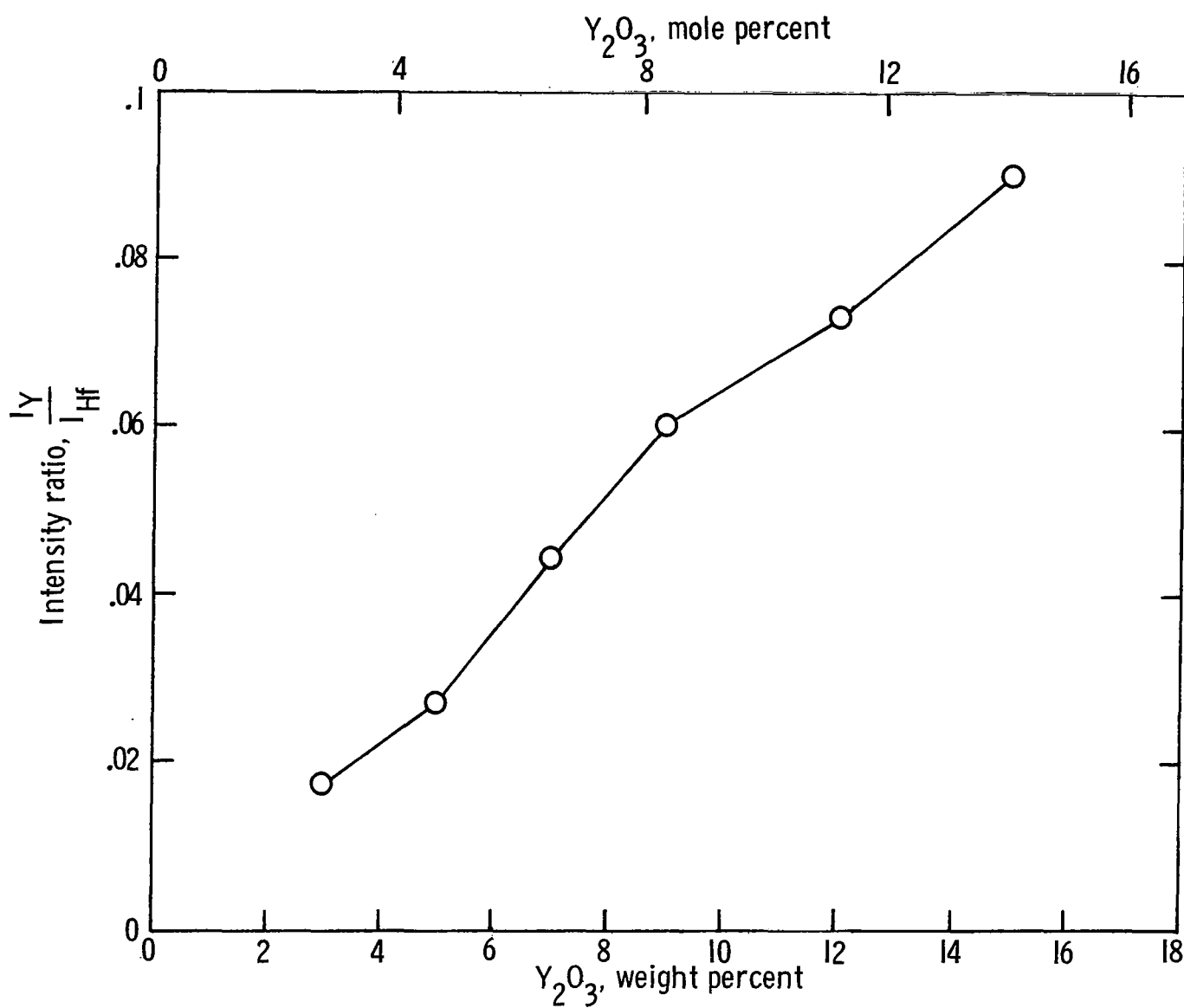


Figure 9.- Standard curve for determination of yttria content in hafnia using X-ray fluorescent analysis.

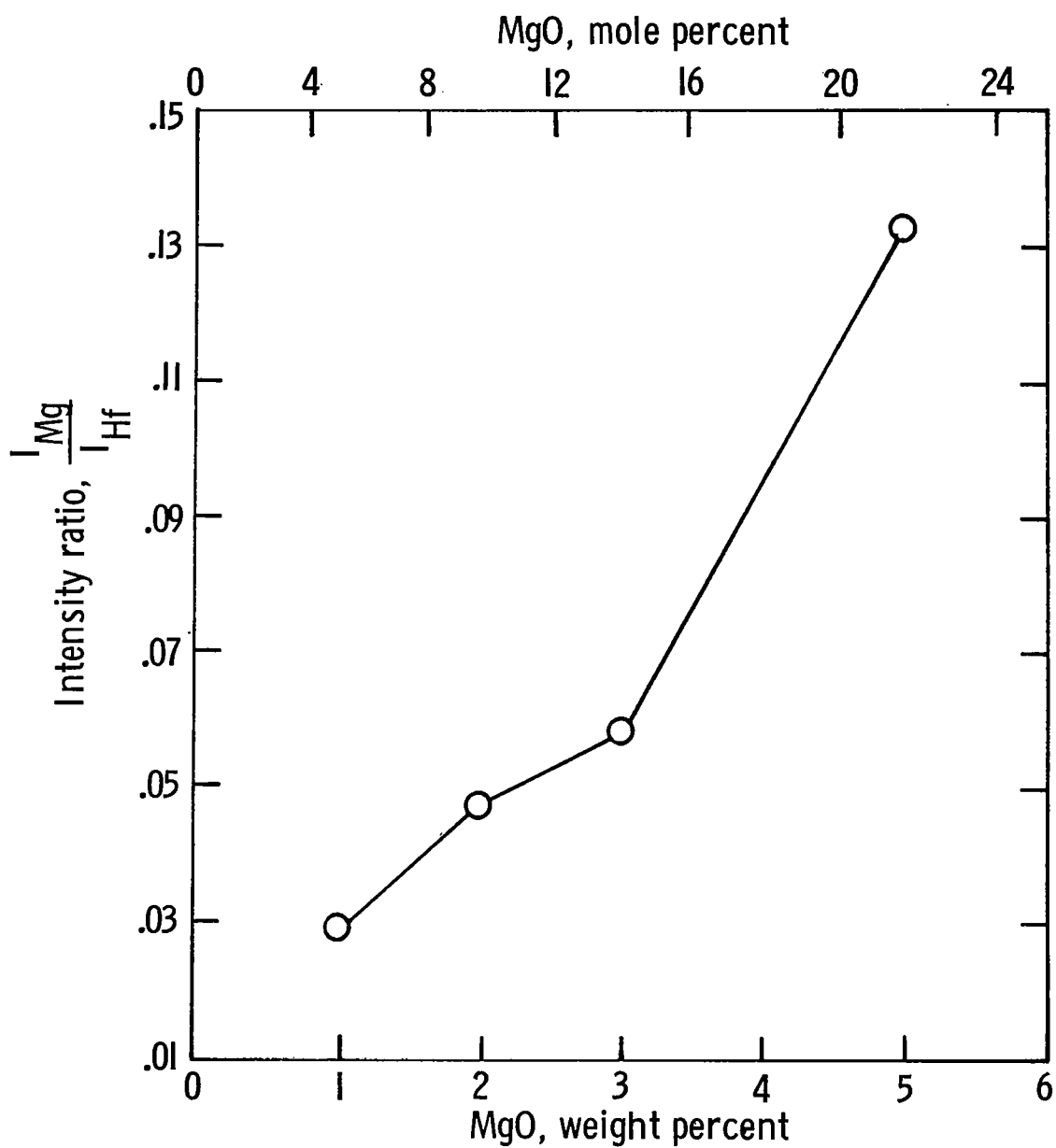


Figure 10.- Standard curve for determination of magnesia in hafnia using electron microprobe X-ray analysis.

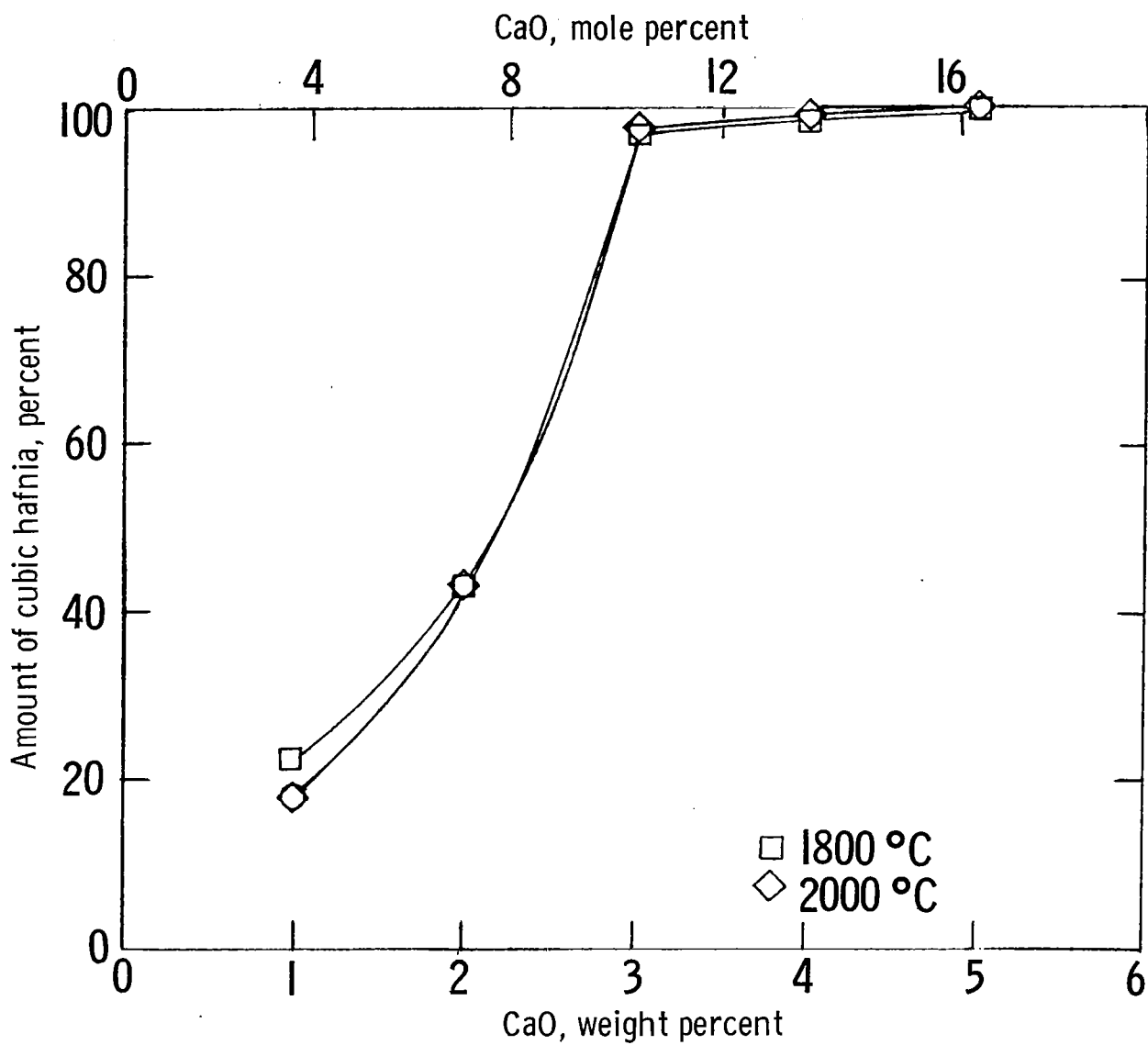


Figure 11.- Percent cubic phase hafnia as a function of calcia additions to monoclinic hafnia sintered for 9 hours at 1800° C (2073° K) and 2000° C (2273° K).

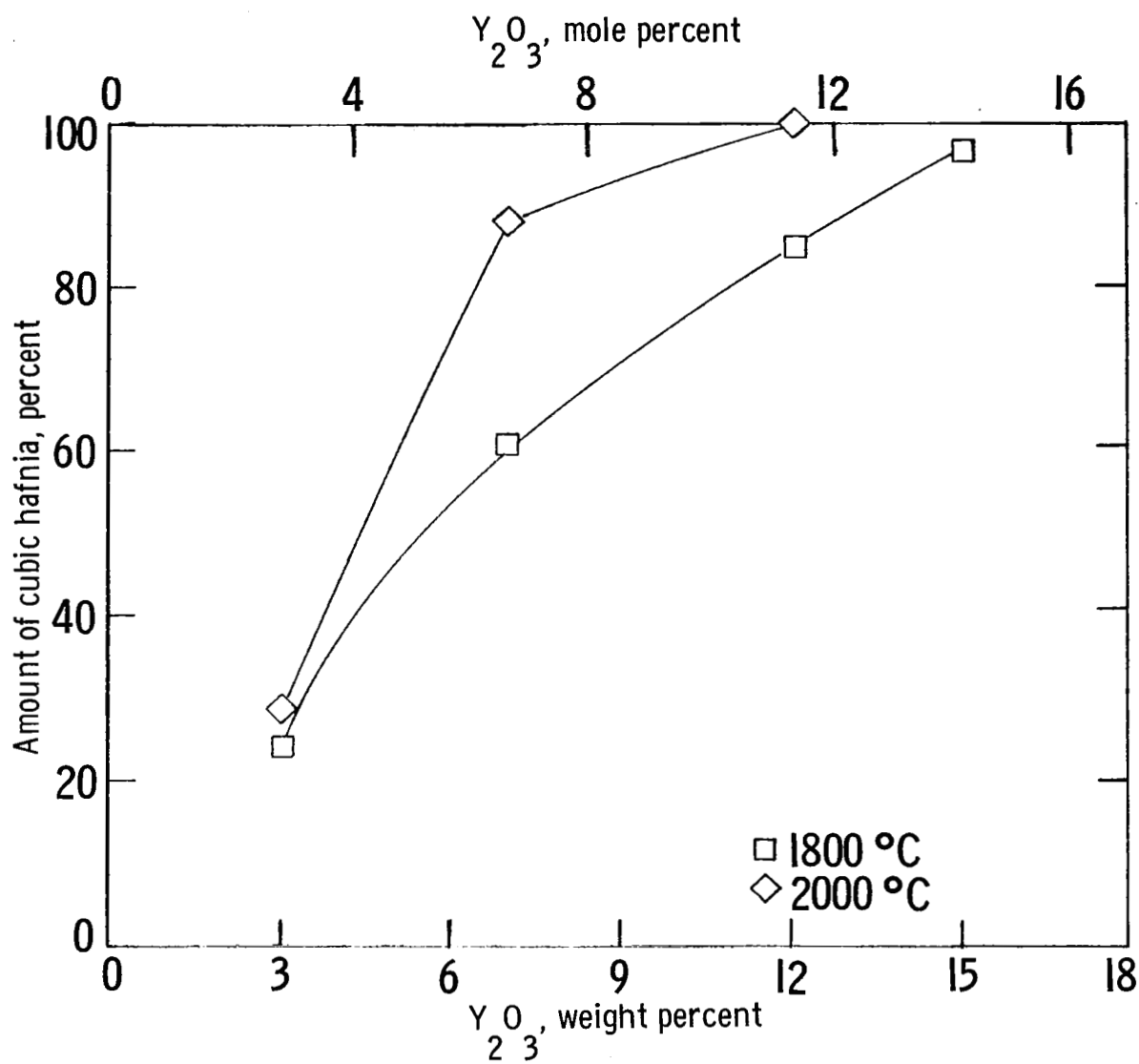


Figure 12.- Percent cubic phase hafnia as a function of yttria additions to monoclinic hafnia sintered for 9 hours at 1800° C (2073° K) and 2000° C (2273° K).

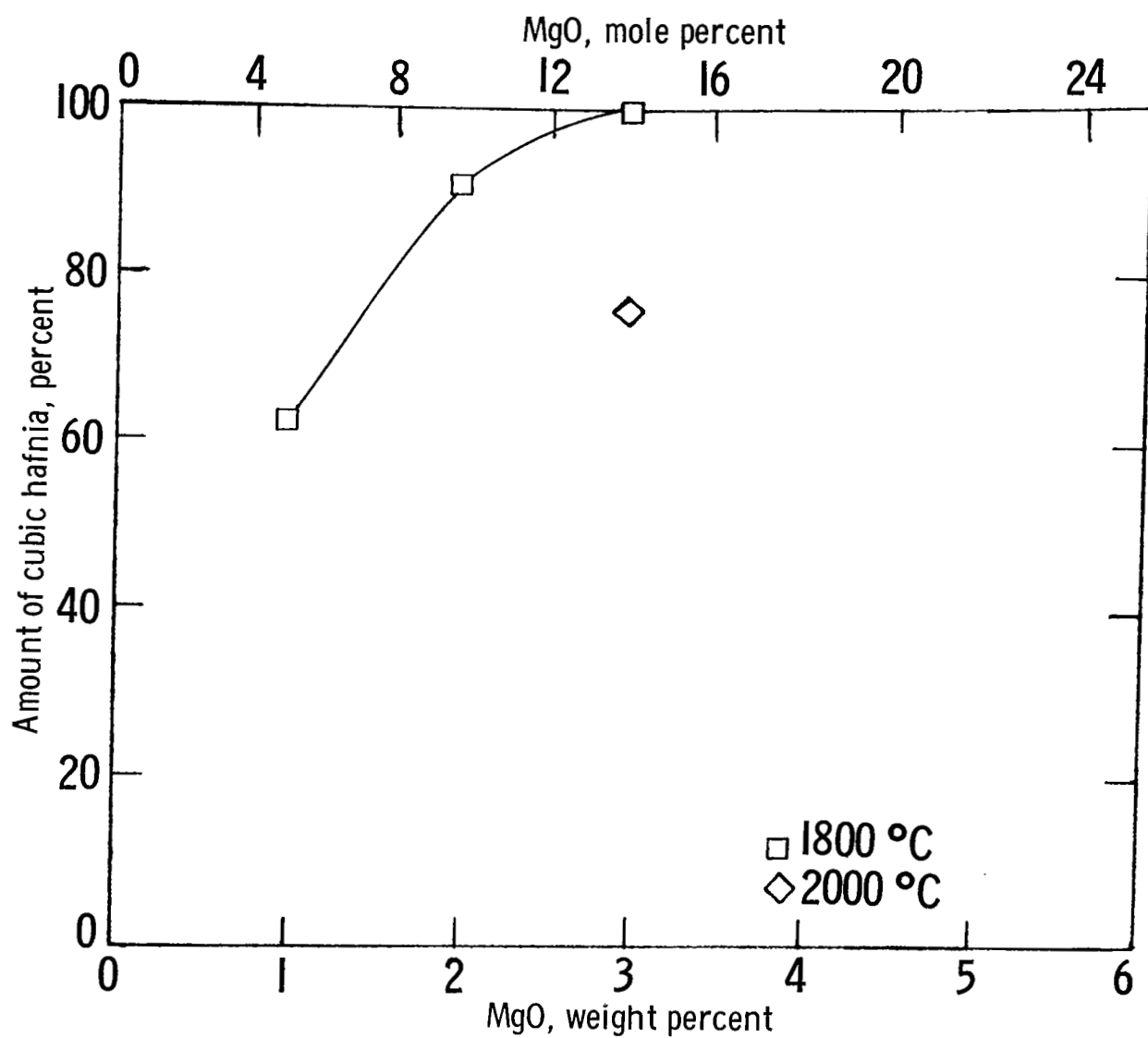
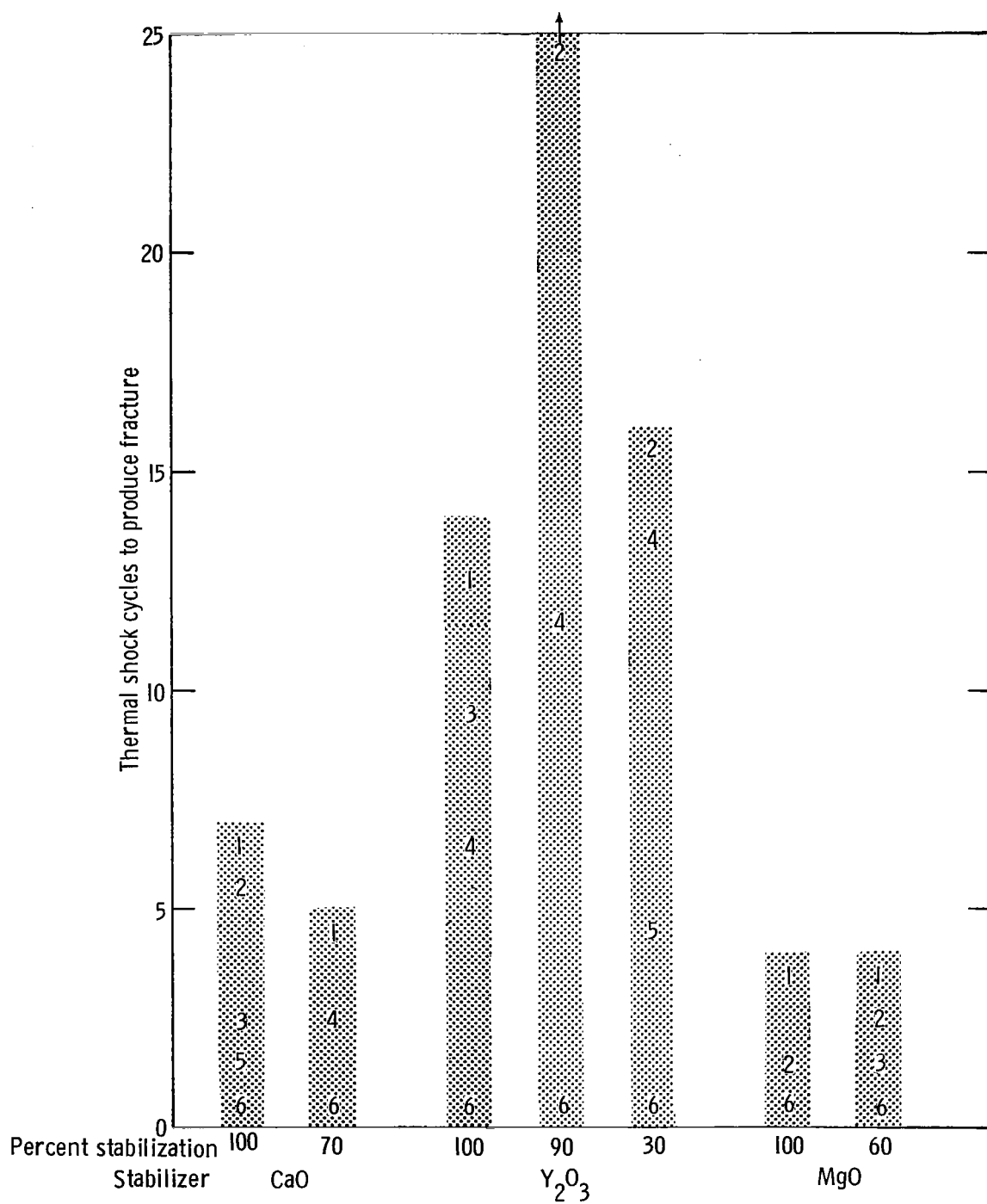
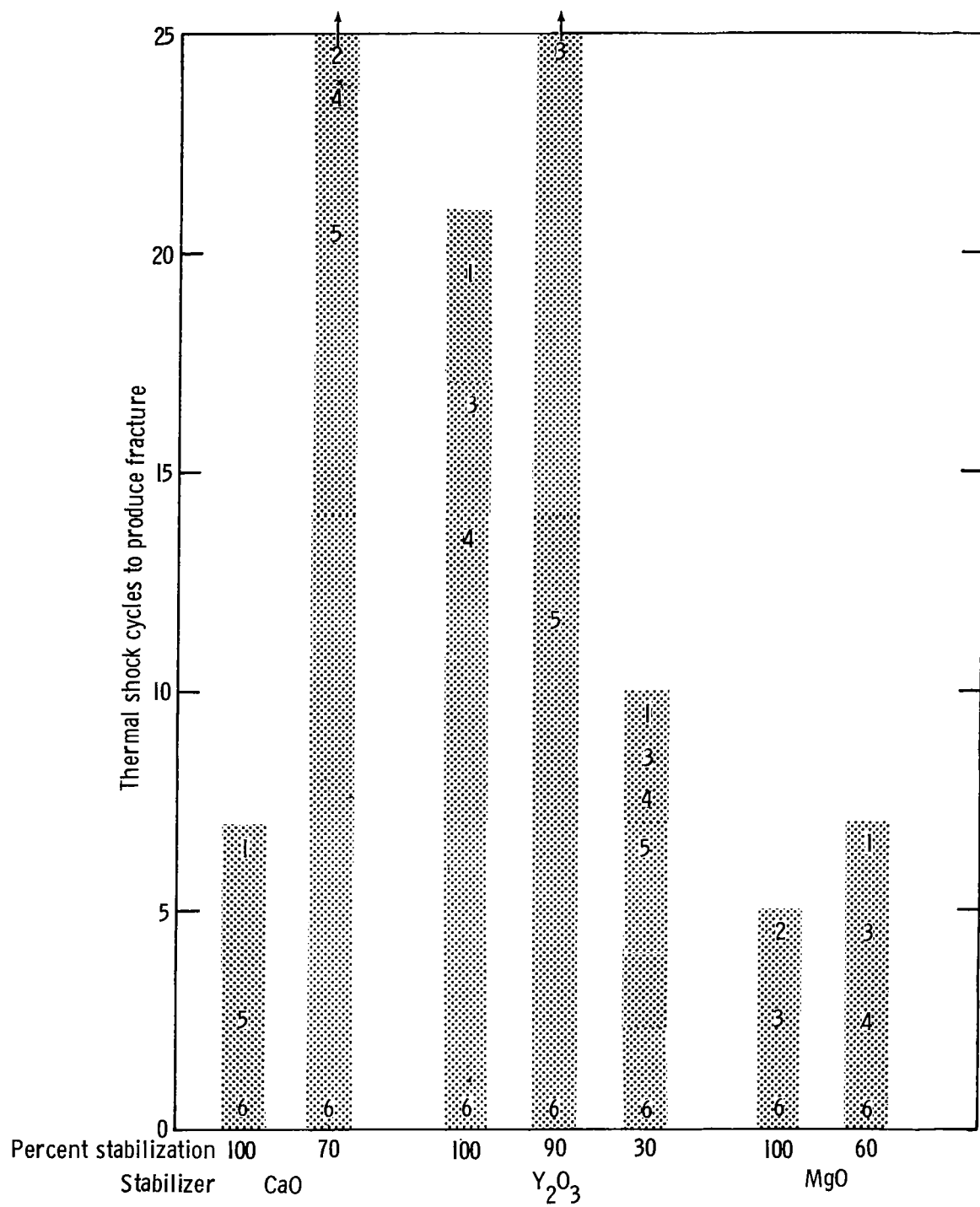


Figure 13.- Percent cubic phase hafnia as a function of magnesia additions to monoclinic hafnia sintered for 9 hours at 1800° C (2073° K) and 2000° C (2273° K).



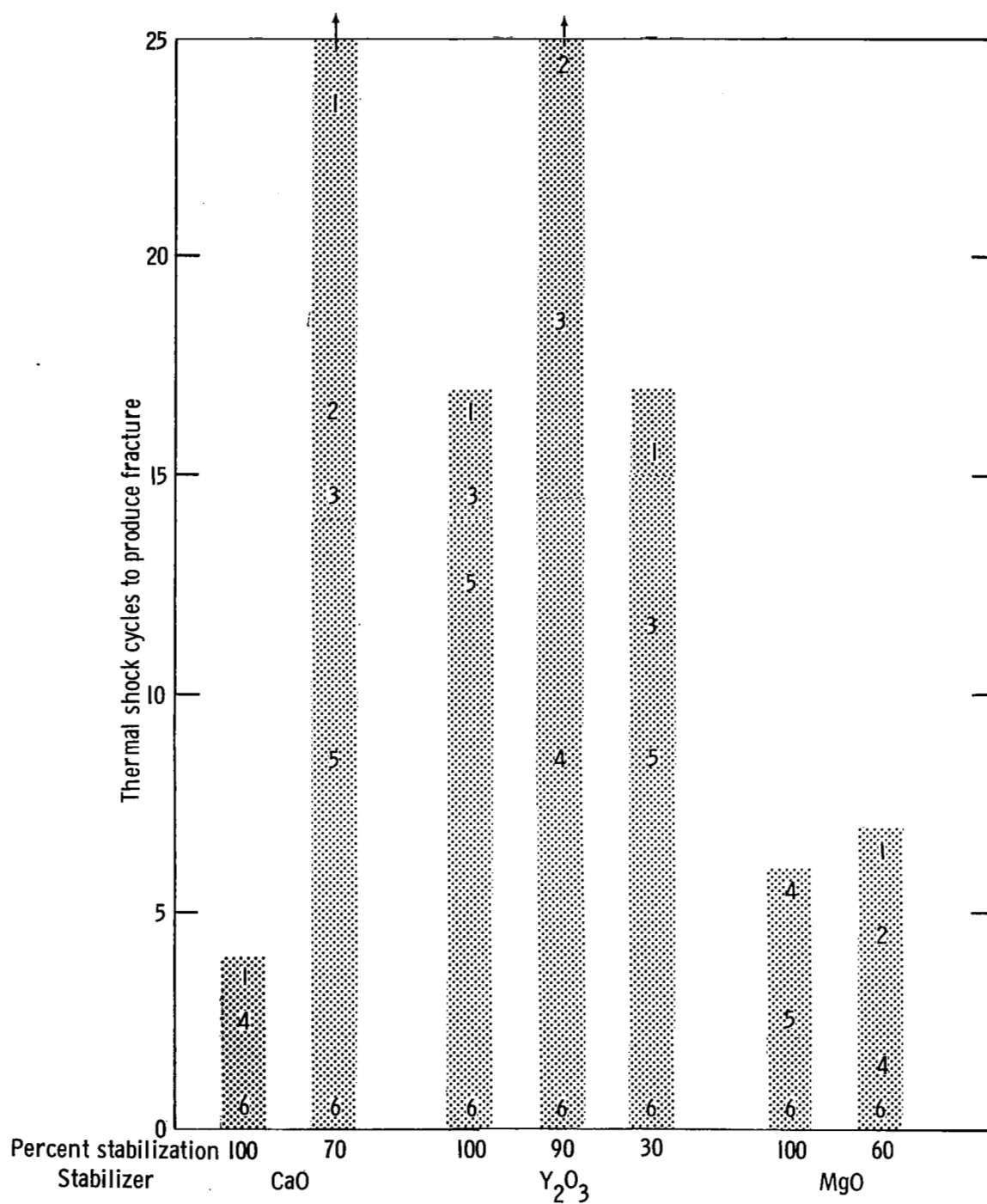
(a) To and from 1040° C (1313° K).

Figure 14.- Thermal-shock resistance of CaO, Y₂O₃, and MgO stabilized hafnia bodies, quick heated and cooled in ambient air. Numbers on bars represent specimens remaining for succeeding tests.



(b) To and from 1750° C (2023° K).

Figure 14.- Continued.



(c) To and from 2000° C (2273° K).

Figure 14.- Concluded.

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